

## MODELING AND SIMULATION OF THE OXIDATIVE DEHYDROGENATION OF ETHANE TO ETHYLENE IN A TURBULENT FLUIDIZED BED REACTOR

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**Abstract:** The present work evaluates the potential use of a fluidized bed reactor on an industrial scale for the production of ethylene through the oxidative dehydrogenation of ethane, with a multimetallic catalyst. For this purpose, a reactor of industrial dimensions operated under turbulent fluidization was modeled and simulated, with a catalyst based on mixed multimetallic oxides (MoVTeNbO). The model contemplates two sequential zones characteristic of these reactors, a dense zone, rich in catalyst particles, followed by a region diluted in catalyst ("freeboard"), and in which a continuous flow of gas and solids is contemplated. The kinetic model used is based on the Eley-Rideal formalism and contemplates a kinetic scheme that considers the oxidative dehydrogenation of ethane to ethylene and the oxidation reactions of these to carbon oxides. Different feed and operating conditions of the reactor were considered, where the operating temperature, the feed composition and the surface velocity of the gas were varied, and the conversion and yields were determined for each case. The results suggest that the oxidative dehydrogenation reaction of ethane has the potential to be carried out at turbulent fluidization conditions at an industrial level, mainly at the high temperature and conversion conditions studied.

**Keywords:** Fluidized bed; Oxidative dehydrogenation; Ethane; Ethylene;

## INTRODUCTION

In the petrochemical industry, ethylene occupies one of the main roles as a building unit for producing a variety of many important chemical compounds. Industry and academia have dedicated efforts to find competitive technological options that allow meeting the growing demand for ethylene through more energy-efficient and environmentally friendly processes than the conventional olefin

production process. In this regard, oxidative dehydrogenation of ethane (ODHE) has been highlighted as one of the most promising alternatives as it has several advantages over the conventional process, such as: not being limited by equilibrium; more energy efficient as it can operate at lower temperatures (below 500°C); fewer side reactions; and, in addition, the deactivation of the catalyst due to coke formation is avoided [1, 2]. Despite the obvious advantages, there are still a couple of challenges to be solved in order to produce ethylene through ODHE: one of them is associated with the design of a selective catalyst to produce ethylene, and the other challenge is related to the design of reactor technology.

There is a variety of catalytic formulations to produce ethylene from ethane, in the presence of oxygen, and among them, the one based on a multimetallic mixture of oxides containing Mo, V, Te and Nb, has stood out for being one of the most active materials, and selective to ethylene, apparently due to the presence of the M1 crystalline phase [3]. With a view to a possible commercial application of this catalytic material for ODHE, it would be pending to conceptualize the design of the catalytic reactor. If the exothermicity of the ODHE reaction is taken into account, due to the inevitable heat released by the reactions of CO and CO<sub>2</sub> formation from ethane and ethylene, the reactor design task turns out to be a complex one.

Ethane/air mixtures can be flammable under certain compositions, so it is risky to operate simultaneously within the flammability limits and above the autoignition temperature. In this regard, at ambient conditions the lower and upper flammability limits of ethane are 2.4 and 16.5%, respectively, the limit concentration of oxygen, 8.7%, and the autoignition temperature 472°C [4, 5] while for ethylene are reported estimated

limit values of 3.45 and 14%, lower and upper, respectively at room temperature [6]. Fluidized beds are one of several reactor options used in industry to carry out gas-solid reactions. A pertinent characteristic of turbulent fluidized bed (TFB) reactors to carry out ODHE is that they have a phase of dispersed solid particles that, in addition to inhibiting the mechanisms that lead to an explosive reaction, also allow operation close to the isothermal.

## METHODOLOGY

In the study of the behavior of a turbulent fluidized bed reactor, to scale, design or even optimize a process, various factors that directly influence its operation must be taken into account (e.g. initial conditions or disturbances). With the purpose of analyzing this behavior, a parametric sensitivity study is carried out to determine the performance of the fluidized bed reactor in turbulent regime on an industrial scale for ODHE using a MoVTenNbO-based catalyst. Among the main variables that affect the behavior of the reactor we have the operating temperature, the concentration of ethane in the feed and the fluidization velocity. Firstly, the results of the simulations of operating the TFB reactor under different temperature values will be presented, avoiding deactivation conditions, interval and concentrations of ethane in the feed, away from flammability risks. Subsequently, the effect of varying the proportions between ethane, oxygen and nitrogen in the reactor feed is evaluated.

*The kinetic model.* With respect to the ODHE reaction, various studies have been reported where the reaction mechanisms considers five main stoichiometric relationships within which the production of ethylene occurs as an intermediate reaction, followed by the subsequent partial and total oxidations of ethylene. (Table 1). In the present work, the parallel and consecutive reactions

of the model are based on the kinetic model proposed by Che-Galicia et al. (2015) [7] developed for ODHE under the Eley-Rideal macrokinetic formalism, for a multimetal oxide catalyst with the presence of Mo, V, Te and Nb.

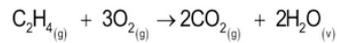
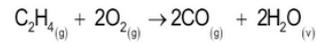
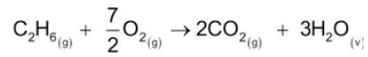
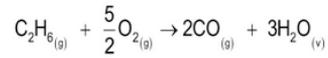
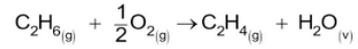


Table 1. Stoichiometric relationships on which the kinetic model used is based.

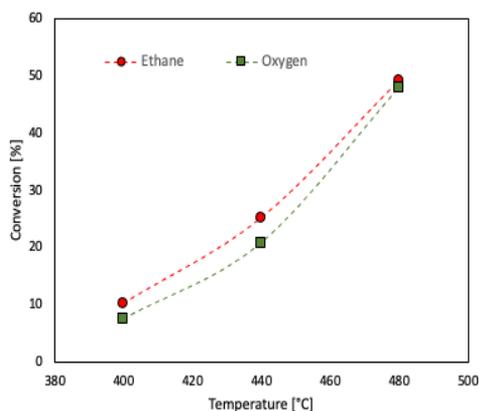
*Reactor model:* The hydrodynamic characteristics of the model corresponds to a reactor that operates in a turbulent regime with a configuration that divides the fluidized bed into a dense bed and a dilute space or “freeboard”. The gas phase approaches plug flow behavior due to the arrangement of the physical structures inside the reactor (e.g. heat exchange tubes, baffles), and as perfect mixing for the solid phase [1]. On the other hand, for the “freeboard”, above the dense bed, both the gas and the entrained solids are described by plug flow behavior. Table 2 presents the dimensions of the simulated industrial reactor and some data on the catalyst used in the model [9].

Variable	Range studied
Reactor height	2.4 m
Reactor diameter	3.0 m
Particle diameter	$9.7 \times 10^{-5}$ m
Void fraction	0.6 – 0.9
Active catalyst mass	18 kg

Table 2: Dimensions of the simulated industrial fluidized bed reactor.

## RESULTS

**Influence of temperature:** Figure 1 presents the predictions of the  $C_2H_6$  and  $O_2$  conversions for ODHE in a TFB reactor at three operating temperatures (400, 440 and 480 °C), for a reaction unit operated with a superficial gas velocity of 0.9 m/s and a feed composition of reactants and  $N_2$  as a diluent with the following molar ratio  $C_2H_6/O_2/N_2 = 9/7/84$ . As shown in Figure 1, for a  $0.28 \text{ g}_{\text{cat}} \text{ h mol}^{-1}_{\text{ethane}}$  space time, ethane conversion increases approximately from 10 to 49%, by incrementing temperature from 400 to 480°C. These results can be compared with the following experimental conversions on which the kinetic expression used in the reactor model is based, that is: 17 to 65% ethane conversion when going from 400 to 480°C, but for a space time of  $23 \text{ g}_{\text{cat}} \text{ h mol}^{-1}_{\text{ethane}}$ . It is clear that the differences between the conversions predicted for the industrial reactor with respect to the experimental laboratory ones are due, among other factors, to the significant difference in the spatial times between both cases.

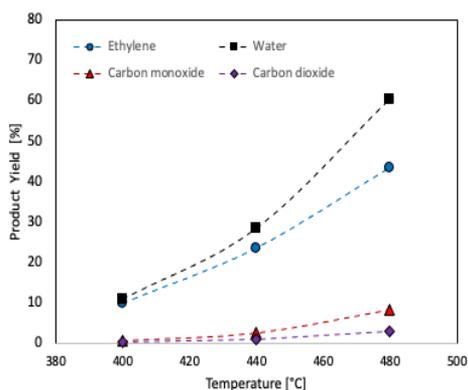


**Figure 1:** Predictions of  $C_2H_6$  and  $O_2$  conversions for the turbulent fluidized bed reactor as a function of temperature. The feed molar ratio was  $C_2H_6/O_2/N_2 = 9/7/84$  and 0.9 m/s the superficial gas velocity.

Regarding the conversions of ethane and oxygen, at low temperatures (i.e. 400 °C) the margin of difference between the conversions

of both species is ca. 5%, being the case in which the conversions achieved were the lowest, within the temperature range analyzed. As the temperature increases this difference decreases significantly to ca. 1% for 480 °C. It is evident that this relative increase in oxygen conversion is associated with the fact that as the temperature increases, the combustion reactions to CO and  $CO_2$  become more significant (see Table 1), which is explained by these reactions having higher activation energies than the reaction of interest. Figure 2 shows the predictions of the yields towards  $C_2H_4$ ,  $H_2O$ , CO and  $CO_2$  from the simulations of a TFB reactor at 0.9 m/s fluidization velocity, where the feed molar ratio was  $C_2H_6/O_2/N_2 = 9/7/84$ , and three reactor temperatures, namely 400, 440 and 480°C. It was found that ethane conversion was the lowest at 400°C, nevertheless, the main reaction occurring appears to be the ODHE to ethylene and comparatively those towards CO and  $CO_2$  are practically negligible. Noteworthy, for the lower temperatures considered carbon oxides yields increased only slightly but occurred at larger rate at the highest reactor temperature. At the temperature of 480 °C both the yields and its difference between products reach a maximum, the former being ca. 43%, 60%, 8% and 3%, for  $C_2H_4$ ,  $H_2O$ , CO and  $CO_2$  respectively. From the perspective of the conversion and distribution of the products, an increase in temperature reveals a positive effect on the yield towards  $C_2H_4$  from  $C_2H_6$ , allowing operation in conditions in which other systems could be at greater operating risk due to limitations associated with heat removal, a problem that in the case of a TFB can be handled in a comparatively more efficiently manner due to the good mixing of solid catalyst particles that characterize them and that allows hot spots to be dissipated and also operate in an essentially isothermal condition.

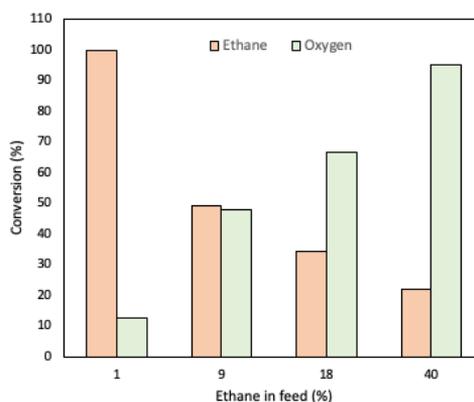
The above suggests that a TFB reactor opens a window of opportunity to operate in regions that have not yet been considered for this catalytic system (called catalyst/reactor). However, the increase in performance towards carbon oxides must be taken into consideration, although it is not considered as a source of deactivation of the catalyst, the mere presence of these is considered negative, either due to an increase in separation costs or due to the production of greenhouse gases.



**Figure 2:** Performance predictions towards  $C_2H_4$ ,  $H_2O$ ,  $CO$  and  $CO_2$  for the turbulent fluidized bed reactor as a function of temperature. It was fed with a molar ratio  $C_2H_6/O_2/N_2 = 9/7/84$  and at 0.9 m/s superficial gas velocity.

**Influence of feed  $C_2H_6/O_2/N_2$  ratios:** Figure 3 shows the predicted  $C_2H_6$  and  $O_2$  conversions for the TFB reactor when considering different inlet ethane concentrations, specifically:  $C_2H_6/O_2/N_2 = 1/7/92$ ;  $9/7/84$ ;  $18/7/75$ ; and  $40/7/53$ , where temperature and superficial gas velocity were maintained constant at 480 °C and 0.9 m/s, respectively. For the case in which ethane is fed at its lowest ratio (i.e. 1% molar  $C_2H_6$ ), its conversion reaches its maximum, while the corresponding  $O_2$  conversion was the lowest observed among the four cases presented in Figure 3 (ca. 16%). It is evident that ethane conversion was reduced as a result of increasing its concentration in the feed, in contrast,  $O_2$  conversions rise in such a way

that they eventually reach scenarios in which it is almost completely consumed (ca. 95%). Such a case corresponds to 40 molar % ethane concentration, which appears to closely delimit the range of operating concentrations, given that oxygen concentration is depleted and the conversion of  $C_2H_6$  reaches its minimum within the range studied. This behavior is somehow expected; reaction environments rich in  $C_2H_6$ , at a given temperature, would promote the conversion of oxygen. Furthermore, for the extreme cases, 1% and 40% ethane in feed, the limiting reactant correspond to  $C_2H_6$  and  $O_2$ , respectively, which corresponds to their nearly complete conversion.

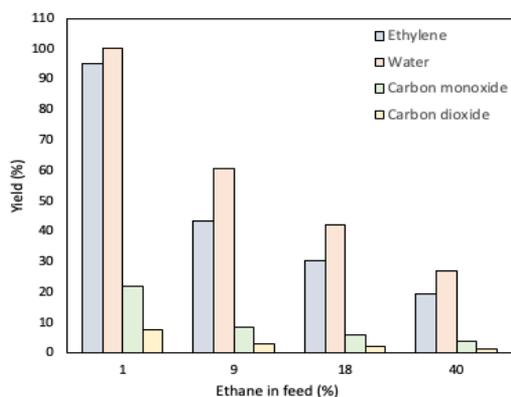


**Figure 3:** Predictions of  $C_2H_6$  and  $O_2$  conversions for the turbulent fluidized bed reactor at different input molar ratios  $C_2H_6/O_2/N_2 = 1/7/92$ ;  $9/7/84$ ;  $18/7/75$ ;  $40/7/53$ . Temperature 480°C and 0.9 m/s gas superficial velocity.

Figure 4 presents the molar yields towards  $C_2H_4$ ,  $H_2O$ ,  $CO$  and  $CO_2$  from the simulations of a TFB reactor for ODHE, at a temperature of 480 °C and a superficial gas velocity of 0.9 m/s for different molar entry ratios (i.e.  $C_2H_6/O_2/N_2 = 1/7/92$ ;  $7/9/84$ ;  $7/18/75$ ; and  $7/40/53$ ). The highest yield to ethylene was observed for 1% ethane molar feed, as for higher ethane concentrations it decreased monotonically. Similar findings were observed for the other three products. From the above results, it

can be pointed out that for the range of temperature and feed ratios considered in this study, those of 480°C and  $C_2H_6/O_2/N_2 = 1/7/92$  are operating conditions for which ethane conversion and ethylene yield were both above 90%.

The percentage yield to CO and  $CO_2$  is affected by the operating conditions, and is favored both by oxygen-rich environments and by an increase in the reactor temperature, with a maximum found for  $C_2H_6/O_2/N_2 = 1/7/92$ . On the other hand, the CO/ $CO_2$  ratio seems to increase with an oxidizing environment, being highest for  $C_2H_6/O_2/N_2 = 1/7/92$  and a temperature of 480°C. With respect to water, it is the main product of the reaction system and it has been reported [10] that it is, among the products, the compound that is mainly adsorbed on the active sites and that is the main factor that affects the reaction rates in the process.



**Figure 4.** Predictions of yields towards  $C_2H_4$ ,  $H_2O$ , CO and  $CO_2$  for the turbulent fluidized bed reactor at different input molar ratios  $C_2H_6/O_2/N_2 = 1/7/92; 9/7/84; 18/7/75; 40/7/53$ . The superficial velocity was 0.9 m/s and the temperature 480°C.

The effect on product yield of increasing  $C_2H_6$  feed concentration and temperature is directly related to the prevailing reactions, that is the oxidative dehydrogenation reaction and the partial and total oxidation reactions. The latter reactions, by which carbon oxides are

formed, are known to be highly exothermic and their presence require adequate heat removal to assure essential temperature control of the reactor and avoid hot-spots in the reactor that can damage the catalyst as well as promote further secondary reactions. There are operating conditions that can place the reactor under such scenarios. For instance, in order to reach high product rates the reactor could be operated under relatively severe conditions, that is at high temperature and high ethane feed concentration (480°C and 40% ethane). High conversions and the related reaction heat released under these conditions can be managed by a turbulent fluidized bed, as heat can be removed by means of a heat exchanger system immersed in the bed and hot-spots are usually dissipated by intense particle mixing characteristic of fluidized bed reactors [11].

## CONCLUSIONS

The operation of an industrial-sized turbulent fluidized bed reactor has been simulated for the oxidative dehydrogenation reaction of ethane to ethylene at different operating conditions. Among the variables evaluated, temperature and ethane concentration in the feed had an opposite effect, since while the conversion of ethane and the yield to ethylene increased with temperature, the opposite resulted from increasing the ethane concentration. On the other hand, an increase in the superficial velocity of the gas reduces the conversion due to an increase in the entrainment of solid catalyst particles out of the bed, and therefore, due to a lower mass of catalyst available for the reaction. The reaction conditions associated with a high conversion and the consequent release of heat are presented as favorable to consider turbulent fluidization, due to its characteristics that facilitate both temperature control and uniformity in the bed.

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